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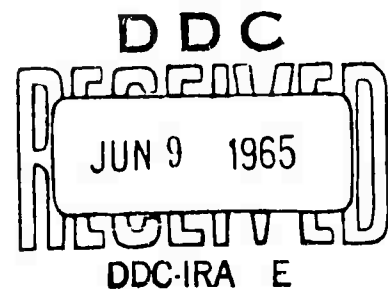
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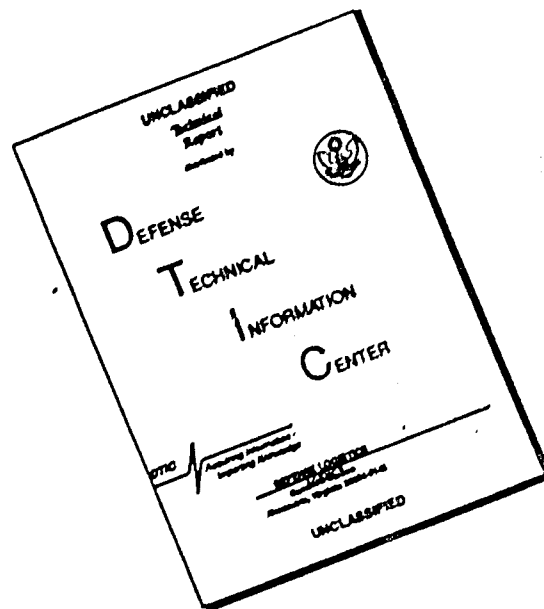


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Exchange and Correlation Effects in an Inhomogeneous Electron Gas*

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ABSTRACT

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. They lead to self-consistent equations analagous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as corrections to the electrostatic potential.

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It has been shown¹ that the ground state energy of an interacting inhomogeneous electron gas in a static potential $v(\underline{r})$ can be written in the form

$$E = \int v(\underline{r}) n(\underline{r}) d\underline{r} + \frac{1}{2} \iint \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + G[n] \quad (1)$$

where $n(\underline{r})$ is the density and $G[n]$ is a universal functional of the density. This expression, furthermore, is a minimum for the correct density function $n(\underline{r})$. In this note we propose an approximation for $G[n]$, which leads to a scheme analogous to Hartree's method but contains the major part of the effects of exchange and correlation.

We first write

$$G[n] \equiv T_s[n] + E_{xc}[n] \quad (2)$$

where $T_s[n]$ is the kinetic energy of a system of non-interacting electrons with density $n(\underline{r})$ ² and $E_{xc}[n]$ is, by our definition, the exchange and correlation energy of an interacting system with density $n(\underline{r})$. For an arbitrary $n(\underline{r})$ one can of course give no simple exact expression for $E_{xc}[n]$. However, if $n(\underline{r})$ is sufficiently slowly varying, we can show¹ that

$$E_{xc}[n] = \int n(\underline{r}) \epsilon_{xc}(n(\underline{r})) d\underline{r} \quad (3)$$

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where $\epsilon_{xc}(n)$ is the exchange and correlation energy per electron of a uniform electron gas of density n . We propose (3) as our approximation even when $n(\underline{r})$ is not slowly varying and shall regard ϵ_{xc} as known from theories of the homogeneous electron gas.³

From the stationary property of (1) we now obtain, subject to the condition

$$\int \delta n(\underline{r}) d\underline{r} = 0, \quad (4)$$

the equation

$$\int \delta n(\underline{r}) \left\{ \varphi(\underline{r}) + \frac{\delta T_s[n]}{\delta n(\underline{r})} + \mu_{xc}(n(\underline{r})) \right\} d\underline{r} = 0; \quad (5)$$

here

$$\varphi(\underline{r}) = v(\underline{r}) + \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' \quad (6)$$

and

$$\mu_{xc}(n) = \frac{d}{dn} (n\epsilon_{xc}(n)) \quad (7)$$

is the exchange and correlation contribution to the chemical potential of a uniform gas of density n .

Eqs. (4) and (5) are precisely the same as one obtains from the theory of ref. 1 when applied to a system of non-interacting electrons, moving in the given potential $\varphi(\underline{r}) + \mu_{xc}(n(\underline{r}))$. Therefore, for given φ and μ , one obtains the $n(\underline{r})$ which satisfies these equations simply by solving the one-particle Schroedinger equation

$$\left\{ -\nabla^2 + \left[\varphi(\underline{r}) + \mu_{xc}(n(\underline{r})) \right] \right\} \psi_i(\underline{r}) = \epsilon_i \psi_i(\underline{r}) \quad (8)$$

and setting

$$n(\underline{r}) = \sum_{i=1}^N |\psi_i(\underline{r})|^2, \quad (9)$$

where N is the number of electrons.

Eqs. (6) - (9) have to be solved self-consistently: One begins with an assumed $n(\underline{r})$, constructs $\phi(\underline{r})$ from (6) and μ_{xc} from (7), and finds a new $n(\underline{r})$ from (8) and (9). The energy is given by

$$E = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \iint \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + \int n(\underline{r}) \left[\epsilon_{xc}(n(\underline{r})) - \mu_{xc}(n(\underline{r})) \right] d\underline{r}. \quad (10)$$

It is physically very satisfactory that μ_{xc} appears in Eq. (8) as an additional effective potential so that differences of μ_{xc} lead to pressures on the electron fluid in a manner familiar from thermodynamics.

The results of this procedure are exact in the following limiting cases: (1) when $n(\underline{r})$ is slowly varying, (2) when ϕ dominates over μ_{xc} (as near an atomic nucleus), and (3) when n is very large.

The method differs from Slater's method of the "exchange hole"⁴ in two ways: (1) Slater's method does not include correlation effects,⁵ and (2) more importantly, the Slater effective exchange potential is $3/2$ of μ_x , the exchange part of the correction potential μ_{xc} in our method. One can verify by a study of the slowly varying case that our result is correct.

It is also possible to obtain a scheme which includes exchange effects exactly, by writing in place of Eq. (3)

$$E_x[n] = E_x[n] + \int d\mathbf{r} n(\mathbf{r}) \epsilon_c(n(\mathbf{r})) \quad (11)$$

where: $E_x[n]$ is the exchange energy in a Hartree-Fock system with density $n(\mathbf{r})$. This leads in place of (8) to a Hartree-Fock type equation.

The same approach, when appropriately extended, also gives simple results for a number of other electronic properties. Among the solid state applications are cohesive energies, elastic constants, Fermi surfaces, electronic specific heat, and energy bands. Details will be given in a future publication.

References:

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3. See for example, E. P. Wigner, Phys. Rev. 46, 1002 (1934); Trans. Faraday Soc., 34, 678 (1938); J. Hubbard, Proc. Roy. Soc. A 243, 336 (1958); P. Nozières and D. Pines, Phys. Rev. 111, 442 (1958); T. Gaskell, Proc. Phys. Soc. (London) 77, 1182 (1961); 80, 1091 (1962).
4. J. C. Slater, Phys. Rev. 81, 385 (1951).
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